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21st European Conference on Fracture, ECF21, 20-24 June 2016, Catania, Italy

# The impact of the multiwall carbon nanotubes on the fatigue properties of adhesive joints of 2024-T3 aluminium alloy subjected to peel

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**Abstract**

The paper presents the results of the research undertaken to determine the impact of the epoxy adhesive nanofiller, in the form of multiwall carbon nanotubes (MWCNT), on the fatigue strength and fatigue lifetime of adhesive joints subjected to peel. Carbon nanotubes were synthesized by means of CVD method with Fe-Co catalysts. Upon the completion of the process, the carbon material was subjected to oxidation and to the acid treatment in order to remove amorphous carbon and catalyst particles. The quantity of 1 wt.% of the dried material was added to epoxy adhesives. Such composition went through the process of mixing, ensuring the adequate nanotubes dispersion. The prepared composition was used to join two elements made of 2024-T3 aluminium alloy.

Adhesive joints underwent high-cycle fatigue peel strength tests with the limit number of cycles of 2 million. The tests were carried out on the electromagnetic vibration inductor with the resonance frequency of the flexible adhesive-joined element of about 600 Hz. For each variant, the fatigue curve and fatigue lifetime were determined for a given level of stress. Thanks to adding carbon nanotubes to epoxy adhesives, the possibility of increasing the fatigue strength by 28.9% and the fatigue lifetime by about 477.2% was discovered. The fatigue strength tests were preceded by static T-peel tests.

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*Keywords:* carbon nanotubes; fatigue; nanofillers; peel; adhesive joints

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10.1016/j.prostr.2016.06.043

## 1. Introduction

The use of adhesive bonding techniques is becoming more commonly used in the branches of industry that require mass reduction in final products while maintaining high strength and stiffness. One of the greatest advantages of adhesive bonds is their ability to connect different materials while ensuring equal stress distribution in the bond and there are no practical limits to the thickness of the bonded elements. Due to this, these techniques are paramount in joining elements in the aerospace industry. Adhesive bonding in aerospace structures may improve aerodynamics, reduce galvanization corrosion due to isolating qualities of adhesives, and does not create heat affected zones, which is a common problem with welded connections. Besides the many benefits of the aforementioned joining technique, there is a demand for research aiming to improve the practical properties of adhesive joints. In truth, there are no problems in achieving relatively high ultimate strength for joints; however, the problem lies in achieving high durability in adhesive joints, which is dependent on multiple factors related to the properties of the composition of the adhesive and the surfaces of adherends.

The best polymer materials for adhesive bonding, with high cohesive performance, are epoxy resin adhesives. Epoxy resin adhesives are substances of low molecular weight with so-called epoxy function, that is, a three-membered oxirane-ring composed of one oxygen atom linked to two carbon atoms. Among the variety of commercially available epoxy compounds, the most important group of epoxy resins is derived from bis-phenol-A. Epoxy resin adhesives are characterized by cohesion strength, long-term durability, and high resistance to ambient conditions and chemicals. Owing to their excellent adhesion properties for metals, mineral surfaces, and wood, they have a wide scope of applications in adhesive technology. Epoxy resin adhesives are cured with primary or secondary diamines. A flexibilizing effect is obtained thanks to the use of longer-chain diamines such as polypropylene glycol diamine, amino-terminated acrylonitrile-butadiene copolymers, and amino amides. According to Pilawka et al. (2011), elastic bonds are obtained thanks to the use of polythiols of higher molecular weight.

Yim et al. (2010) reported that in recent years, conductive-filler-filled polymeric composites have been used for a wide range of applications due to their versatile properties, including thermal stability, mechanical strength, electrical resistance, and adhesive characteristics. Gojny et al. (2005) reported that of these composites, the isotropically conductive adhesives (ICAs) filled with organic or inorganic fillers have been investigated as a lead-free alternative in microelectronic packaging. A number of techniques have been considered to improve the mechanical properties of structural adhesives containing fillers such as carbon, nylon, or glass micro- or nano-fibres. As noticed Wernik et al. (2015) and Gkikas et al. (2012), with the passage of time, the manufacturing of modern composites has begun to shift from micro-scale composites to nanocomposites thanks to the use of the unique combination of mechanical and physical properties of nanofillers with a characteristic dimension below 100 nm, especially nanofillers based on carbon nanotubes (CNTs).

Recent studies show that the scientific community is adopting a variety of different methods to develop nano-reinforced composites with varying levels of success. Liu et al. (2010) and Sahoo et al. (2009) showed that the properties of CNT-based nanocomposites are influenced by a number of factors that include the CNT synthesis and purification process, the geometrical and structural properties of CNTs, their alignment in the matrix, the dispersion process, and the fabrication process.

The most commonly used engineering materials in aerospace are aluminium alloys due to their wide range of advantages. First of all, they are characterized by a very low density and the ability to transfer loads in load carrying parts, while still being cheaper than other light alloys like those made of titanium and magnesium (Packham et al. (1995)). Many construction solutions rely on joining of these materials through the use adhesives. There has been a vast amount of research dedicated to various methods of preparing aluminium alloy joints for the static strength of adhesive joints. However, there are few scholarly articles dedicated to the fatigue strength of these bonds. The fatigue strength of a correctly prepared joint depends especially on the type of adhesive as well as load ratio - R, the ratio of minimum to maximum value of load.

Elkadi et al. (1994) and Mandell et al. (1983) revealed that the effect of load ratio has been found to be significant in the fatigue response of polymeric materials. Underhill et al. (2006) observed that increasing the load ratio for a constant maximum fatigue load increased the fatigue life and, conversely, for a constant load range, an increased load ratio had a deleterious influence on the fatigue response. However, Crocombe et al. (1999) found that the effect of frequency on fatigue strength of adhesively bonded joints to be less important.

## 2. Materials and method

The CNTs used in the experiments were produced in the laboratory with the use of the CVD method. To achieve this aim, ethylene, as the source of carbon, was decomposed on the Fe-Co (1:1) catalyst. The nanocrystalline Fe-Co catalyst was obtained by co-precipitation of hydroxides starting from a solution of corresponding nitrates and using ammonia water as a precipitating agent. A small amount of calcium and aluminium nitrate was also added to the reaction mixture to reach final concentrations of both CaO and $Al_2O_3$ of below 3 wt.% in the catalyst.

The final Fe-Co catalyst was obtained after reduction with hydrogen at 400 ºC. After the reduction, the calcium and aluminium oxides remained in the oxide state and played the role of structural promoters of the catalyst, preventing the sintering of small nanocrystallites of cobalt and iron at high temperatures. The addition of such structural promoters was necessary, as the decomposition of ethylene was carried out at 700 ºC.

The material obtained after the decomposition of ethylene on the Fe-Co catalyst was oxidized in air at 400 ºC for 1 h to remove amorphous carbon and then treated with concentrated hydrochloric acid (1 M) in a microwave-assisted hydrothermal reactor at a pressure of 30 MPa for 1 h to remove catalyst particles. After the acid treatment, the samples were filtered, washed with distilled water, and dried at 130 ºC.

The efficiency of the applied purification method was assessed with the thermogravimetric method using DTA-Q600 SDT equipment (TA Instruments). The applied heating rate was 10 ºC/min, starting from room temperature and rising to 900 ºC in air.

The content of metal in the final product was at the level of 3 wt.%. The external diameter of MWCNTs was about 40 nm.

Two kinds of epoxy adhesives were used in the research: Bison Epoxy adhesive, supplied by Bison International B.V. and Epidian 57 epoxy resin with PAC hardener, supplied by CIECH Sarzyna S.A.

Static strength tests were conducted by the T-peel test for the specimens presented in Fig. 1. On the other hand, fatigue tests were conducted with the use of the specimens presented in Fig. 2. The adherends for both specimen variants were made of 2024-T3 aluminium alloy. A variety of methods of surface preparation were used prior to bonding process. The preferred method of preparing the surface for all of the variants was sand blasting; however, sand blasting caused bending in the case of the sheet metal used for the static strength tests. As a result, surface grinding, with the use of a non-woven fabric grinding wheel on a mandrel, was done instead for these samples. The surfaces of the adherends used in the fatigue tests were sand blasting with aloxite 95A under the following conditions: grain size $w_z$ = 0.27 mm, air pressure $p$ = (0.8 ± 0.1) MPa, and blasting time $t$ = 60 s. Immediately after that, the adherends were placed in a container with acetone in order to protect them from oxidation and they were stored there until bonding.

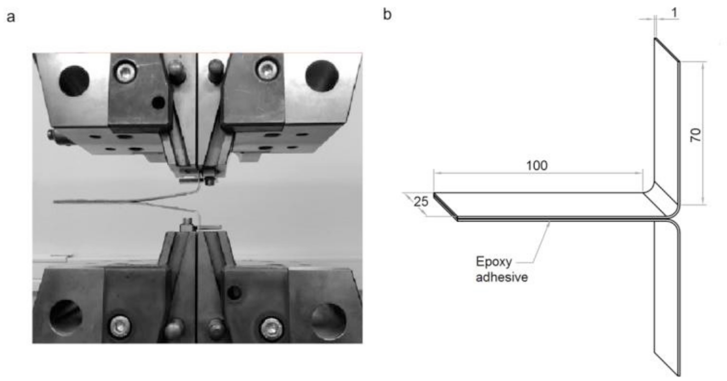


Fig. 1. A joint specimen mounted on the testing machine (a) and dimensions (b) of sample used in static T-peel testing.

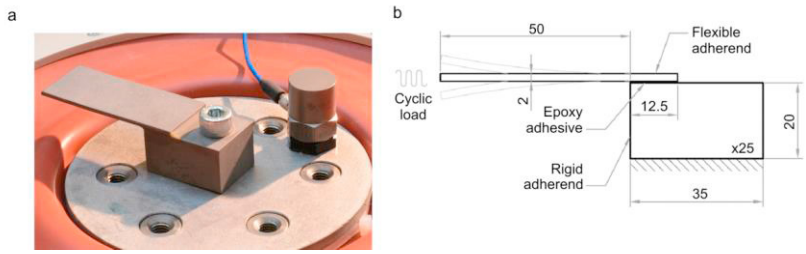


Fig. 2. A joint specimen mounted on the shaker (a) and dimensions (b) of sample used in peel fatigue strength testing.

The adhesive compositions with CNTs were prepared in the following sequential stages:

- the epoxy resin was heated up to 50 °C in order to reduce its viscosity
  the purified CNTs were added to the epoxy resins
- mechanical and ultrasonic mixing of the resin with the nanofiller was carried out at a constant temperature of 50 °C for 60 minutes
- after cooling, the right amount of hardener was added and mixed mechanically for 2 minutes

The hardening process of the adhesive-bonded joints lasted 24h at room temperature (20 ± 3 °C) under a constant pressure of 0.1 MPa applied to the joint area.

The fatigue strength tests were applied to the specimens according to the following variants:

- variant B_neat: the specimens were bonded with the Bison Epoxy adhesive composition (proportion: 100 parts by weight of the hardener per 100 parts by weight of the resin)
- variant B+1%MWCNT: the Bison Epoxy adhesive composition was the same as above, but 1 wt.% of MWCNTs was added
- variant E_neat: to glue the specimens, the Epidian 57 adhesive composition was used with PAC hardener (proportion: 80 parts by weight of the hardener per 100 parts by weight of the resin)
- variant E+1%MWCNT: to the composition described above, 1 wt.% of the filler was added in the form MWCNTs

This 1 wt.% MWCNT loading was chosen on the basis of the recommended loading by Breton et al. (2002) and Allaouia et al. (2002).

The static strength test, that were done with the use of the T-peel test method, was conducted on a Zwick Z100 machine with a displacement rate of 10 mm/min at room temperature. Two values were recorded for every sample, namely peak load/force to initiate failure and average peeling force. Four repetitions were done for each variant.

Fatigue tests were conducted with the use of the original methodology developed by the authors, which is a convenient and relatively fast high-cycle fatigue strength test method for testing the peeling of adhesive joints at a resonance frequency of specimen. Fatigue tests system was presented in Fig. 3.

The tests were done on the vibration test system TiraVib TV 50350 LS 120 which consists of: the vibration exciter S 50350-120, the amplifier A1 01 1 004.

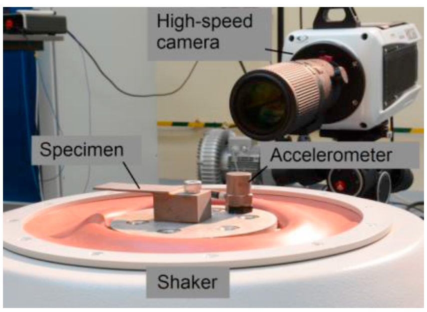


Fig. 3. Photo of the fatigue tests system.

The objective of the research was to evaluate the impact of the above-described type of epoxy adhesive filled by MWCNT on the fatigue strength of an adhesive joint subjected to peel loading at the limit number of cycles, $2 \times 10^6$. The performed tests were in fact the accelerated measurements of fatigue strength in a symmetrical (oscillating) stress cycle.

Specimens for each variant were subjected to resonance vibrations at four different amplitude levels. The number of cycles was counted up to the point when it was no longer possible to maintain the vibrations of the specimen at a given amplitude level, which was the evidence of destruction. For every level, the tests were repeated four times. The lowest level of the dynamic load was the value at which the specimen did not fail after being loaded by $2 \times 10^6$ cycles.

The amplitude of the end of the flexible adherend was measured using a high speed camera Phantom v711 (Fig. 3). This amplitude value was correlated to the maximum normal stress in the adhesive joint by FEM analysis.

## 3. Results and discussion

The results of T-peel static strength tests are listed in table 2. The experiment shows that for every joint variant with the nanofiller, the value of the peak load is significantly greater in comparison to the basic variant – without a filler. Meanwhile, this tendency is reversed in later stages where the average peeling force is greater for the basic variant (B_neat and E_neat).

Table 1. Results of T-peel tests.

| Variant of joint | Peak load (*N*) (SD) | Average peeling force (*N*) (SD) |
|---|---|---|
| B_neat | 71.73 (6.93) | 38.72 (4.46) |
| B+1%MWCNT | 84.92 (14.38) | 31.25 (6.87) |
| E_neat | 87.36 (9.11) | 46.27 (4.65) |
| E+1%MWCNT | 101.75 (16.48) | 34.12 (8.91) |

The graphs plotted during T-peel tests for variants with and without nanofiller were compared (Fig. 4). The differences in the shape of the curves may suggest that adding nanofiller in the form of MWCNT has an impact on the increase in the stiffness of adhesive composition.

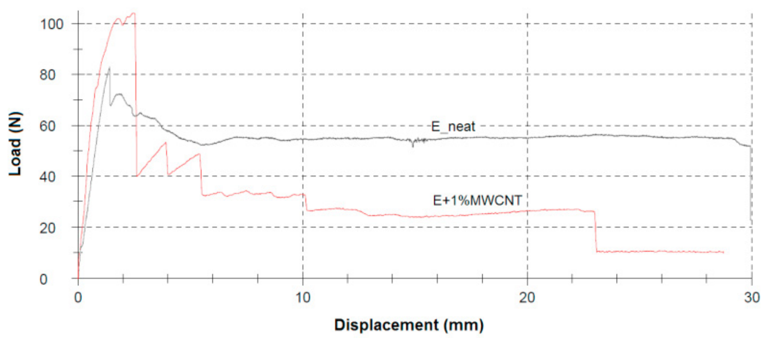


Fig. 4. Load-displacement curves from T-peel tests.

When conducting fatigue strength tests, it was observed that the value of the resonance frequency of the specimen is dependent to degree of joint fatigue failure. Two stages can be differentiated. During the first stage, the value of the resonance frequency decreases slowly, which is related to the fatigue of the face joint. In the final stage, there is quick decrease in resonance frequency prior to failure until it is impossible to maintain the vibrations at a constant amplitude. At this stage, the joint is destroyed to such a degree that even when small force is applied, the joint will split.

The results of the fatigue strength tests show that it is possible to improve the fatigue properties of adhesive joints thanks to the use of MWCNTs as fillers for epoxy adhesives in the considered amount of 1 wt.% of MWCNTs. Fig. 6 and Fig. 7 demonstrates the comparison of the fatigue curves for the basic variants and those with nanofillers.

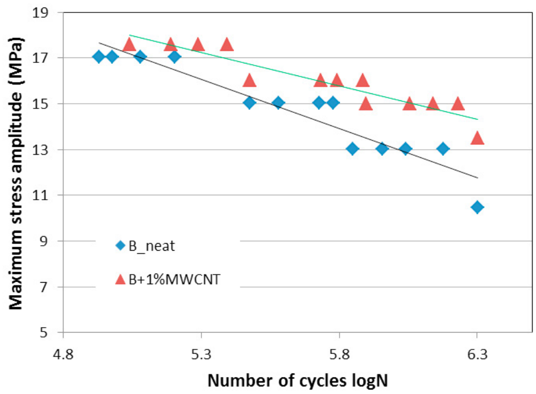


Fig. 6. Comparison of fatigue curves for Bison Epoxy variants.

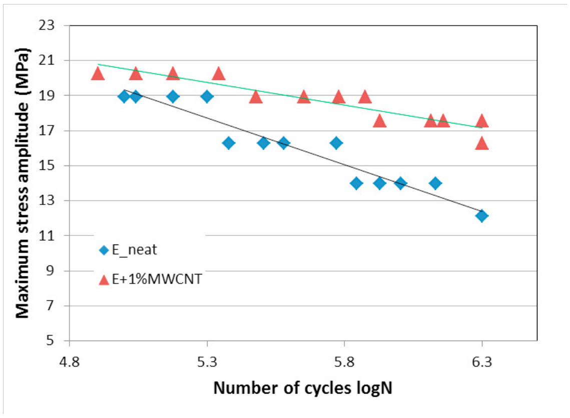


Fig. 7. Comparison of fatigue curves for Epidian 57/PAC variants.

In the case of the Epidian 57 adhesive composition with the PAC hardener filled by 1 wt.% MWCNTs, the fatigue strength increased from 12.43 to 16.04 MPa (an increase by 28.9%) compared to E_neat variant. The research also revealed a similar increase of fatigue strength in the case of Bison Epoxy adhesive: from 10.68 to 13.5 MPa for B+1%MWCNT variant (an increase by 26.5%).

The results of fatigue tests confirmed that it is possible to significantly improve the fatigue lifetime; for example, in the case of E+1%MWCNT variant at the stress amplitude of 17.9 MPa, a more than fourfold increase in the fatigue lifetime was obtained from 199000 to 1150000 cycles (an increase of 477.2%). For the Bison Epoxy adhesive composition and the stress amplitude of 15.3 MPa, the fatigue lifetime was increased by 213.8% (from 316000 to 989500 cycles) by the introduction of MWCNTs.

Fig. 8 demonstrates SEM micrographs of exemplary fatigue fractures, while Fig. 9 presents SEM micrograph of cured Epidian 57/PAC adhesive with visible carbon nanotubes. The images of surfaces from fatigue tests show a noticeable difference in fracture morphology between the neat adhesive and nanotube-reinforced adhesive. The material with neat epoxy typically exhibits a smoother fracture surface than the material with nanotubes reinforcing the matrix.

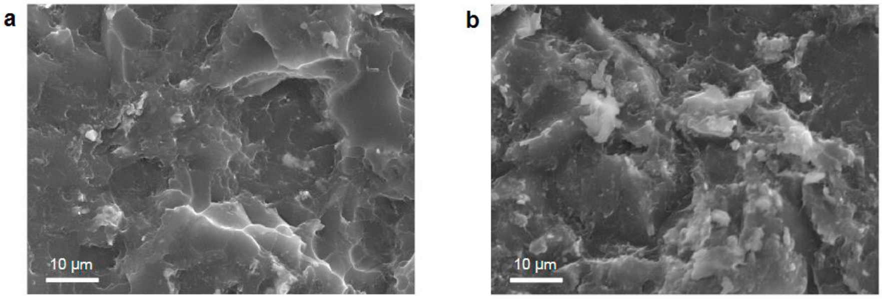


Fig. 8. Scanning electron micrographs of representative fracture surfaces from fatigue tests (a) for E_neat variant; (b) for E+1%MWCNT variant.

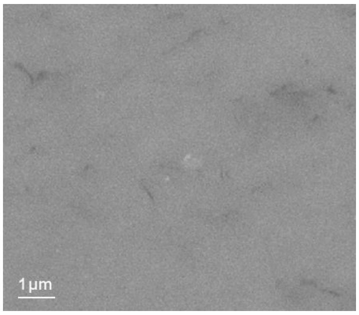


Fig. 9. SEM image of 1 wt.% MWCNT in Epidian 57/PAC epoxy adhesive.

The possibility of improving the strength properties at variable cyclic loads by means of nanofillers, in this case the MWCNTs, was confirmed.

Barber et al. (2003) explain that the mechanism of improvement of some mechanical properties by means of MWCNTs in epoxy matrix is related to the phenomenon of CNTs, whose addition provides an additional source of energy absorption. Gojny et al. (2005) and Singh et al. (2015) revealed that the Multi-walled nanotubes absorb more energy, which is dissipated within the area of nanotubes and takes more time to penetrate the specimen area.

Ganguli et al. (2005) said that It is believed that the randomly oriented MWCNTs are responsible for such high resistance to separation of the MWCNT composites. The increased number of features on the surface (ridges) gives rise to a greater area for the absorption of the fracture energy, thus giving rise to higher values of toughness. Hedia et al. (2006) showed that the inclusion of the organic MWCNTs gives rise to mechanical reinforcement at the molecular level. What is more, the enhanced contact between the fillers and the resin results in better bonding, thus restricting the crack propagation path.

Barber et al. (2003) focused on the measurement of a single MWCNT and the strength of the polymer matrix joint. They proved that the value of separation stress is relatively high, which indicates the existence of both chemical and physical interactions in the bonding model. This confirms that the above-mentioned mechanisms of nanotube pull-out and crack bridging are effective and provide improvements of fatigue strength.

## 4. Conclusions

This paper offers an experimental insight into the fatigue strength properties of three epoxy adhesive polymers containing multi-walled CNTs. The results of the experiment clearly suggest that the addition of MWCNT fillers to epoxy adhesives makes it possible to improve the properties of reinforced epoxy adhesives such as fatigue strength properties and their fatigue lifetimes.

Despite the fact that the use of CNTs is still not a common practice, because of the high cost of fabrication, the ongoing research into less expensive manufacturing techniques lets us assume that this type of material will be widely used in the future to improve the strength properties of bonded structural joints. The results of the research presented in this paper show that nanotechnology can contribute to the improvement and, therefore, more common use of adhesive-bonded structures.

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